**Summary Report**

The objective of the action was to study the silicon analogue of graphene, silicene, with a specific focus on growing a doped silicene layer, ideally preparing it onto substrates not yet achieved in the past (e.g. europium and boron nitride) but also designing strategies to decouple it from the underlying metal substrate. To this end the first envisaged step was to attempt to grow silicene on the Ag(111) surface, which could serve as a reference due to the big amount of published work available. Since the strong interaction and hybridization between silicene and Ag(111) is known to be detrimental to the electronic properties of the as-yet unseen free-standing silicene layer, it was aimed to exploit the interaction with adsorbed functional organic molecules (such as metallo-porphyrins) as a way to reduce the strength of the silicene-Ag(111) interaction. In this regard, angle-resolved photoemission spectroscopy (ARPES) measurements were planned for the first six months of the project, to verify the effect of molecular properties on the electronic structure of Ag-supported silicene.

However, due to the offer of a permanent position at another institution, the fellow ended the fellowship prematurely after three months. As the difficulties and time scales involved with *in situ* ultra high vacuum measurements are quite severe, it merely possible in the first three month to start preliminary activities for SiliNano project – specifically this realitevely short period is not suitable for developing novel growth recipes from scratch. This is in line with the original proposal, the initial phase was set aside for preparative studies, such as reproducing results from the literature. Thus the experimental time available could be successfully employed to set up the experimental apparatus at TUM was for the acquisition of ARPES data. Moreover, we developed a strategy to use metal-ribbon evaporators for the *in situ* deposition of semiconductor materials such as Si and Ge under ultra high vacuum conditions and with negligible contamination. In parallel, temperature-programmed studies (temperature-dependent X-ray photoelectron spectroscopy and temperature programmed desorption) on metallo-porphyrins adsorbed on Ag(111) and thymine adsorbed on TiO2(110) (the latter being a system with potential applications for improving the biocompatibility of medical implants, the former for the development of single-site heterogeneous catalysts) were pursued. Importantly, the successful upgrade of the experimental setup and the development of a standard acquisition protocol for performing temperature-dependent photoemission experiments were regarded as a crucial step for the silicene project enabling to identify the most suitable growth conditions and to understand the related surface chemistry.

Additionally the applicant used the initial three month period of the fellowship to apply for beamtime at synchrotron light sources in order to study a closely related system, the functionalization of graphene on an iridium substrate by intercalation of cobalt. Moreover, during an already awarded beam time at the Berlin synchrotron, BESSY II, the applicant studied, in collaboration with Dr. M. Lackinger (TUM Munich and Oskar-von-Miller Lehrstuhl für Wissenschaftskommunikation, Deutsches Museum) the formation of related other covalent 2D-sheet networks using temperature programmed X-ray photoelectron spectroscopy. The focus of this study was to understand the formation of the 2D layer as a function of molecular and co-deposited catalyst coverage. Understanding how such layers grow is fundamental to developing 2D layers with the high quality and sheet size necessary to be useful on an industrial scale. After the end of the fellowship period the fellow has also applied for beam time, in 2016, to study the adsorption of molecules on another 2D layer, boron nitride, as well as the aforementioned graphene study.

**Milestones**

The first milestone of the proposed SiliNano project was to “pursue the preparation of silicene on Ag(110) and Ag(111), and characterise the prepared layers using electron based techniques (LEED, XPS, in-lab ARPES)”, however due to the early termination of the fellowship it was not possible to fully achieve this milestone, although important experimental progress was achieved.

**Ethical Issues**

None

**Critical implementation risks and mitigation measures**

As the project has now ended there is no need to mitigate any future risks associated with the project.

**Dissemination and exploitation of results**

The main work from the three month period of the fellowship, the temperature programmed study of thymine on TiO2(110) and the synchrotron experiments on 2D covalent networks will be published in due course.

Manuscripts in preparation:

* *Stable bi-layer adsorption of thymine on TiO2(110)*, D. A. Duncan, P. S. Deimel, J. Pfisterer, M. Friton, P. Feulner, R. Acres, F. Allegretti and J. V. Barth
* *Oxidation of Cr-TPP on Ag(111)*, P. S. Deimel, P. C. Aguilar, M. Paszkiewicz, P. Feulner, D. A. Duncan, F. Allegretti and J. V. Barth
* *Exploiting metal-organic bond and their catalytic activity for higher quality 2D covalent networks*, M. Friton, A. Rastgoo, D. A. Duncan, P. S. Deimel, F. Allegretti, M. Lackinger
* *Spin resolved charge transfer through an organic layer*, T. Sundermann, P. S. Deimel, D. A. Duncan, F. Allegretti, P. Feulner, U. Heinzmann
* *Adsorption of freebase corrole on Ag(111)* M. Paszkiewicz, Y. Zhang, P. S. Deimel, D. A. Duncan, F. Allegretti, J. V. Barth and F. Klappenberger

**Dissemination and communication activities**

Participation in conferences :

* Contributed an oral presentation to the Deutsche Physikalische Gesellschaft (DPG) annual meeting in Berlin
* Presented poster at the Menzel symposium “Present Challenges in Surface Science and Photon-Driven Phenomena at Interfaces” in Munich, Germany
* Contributed an oral presentation to the European Conference on Surface Crystallography and Dynamics-12 (ECSCD-12) in Trieste, Italy

**Intellectual property rights resulting from the project**

There are no intellectual property rights involved with the project.

**Innovation**

The terms outlaid in the documentation do not apply to this project as there is no industrial partner, nor medical application for this work.

**Open research Data**

The data will be deposited in a suitable repository after it has been published in peer reviewed journals.

**Work and Overview of Progress**

During the three month period temperature-dependent X-ray photoelectron spectroscopy (TD-XPS) and temperature programmed desorption (TPD) measurements were acquired for thymine on titanium dioxide TiO2(110). In previous measurements by the fellow it was observed that, upon adsorption on the surface, the thymine spontaneously formed a bilayer structure even at submonolayer coverages. It was also observed that annealing the sample to ~450 K resulted in the removal of the second layer leaving an intact single layer. Additional heating resulted in the deprotonation of one of the nitrogen atoms in the thymine molecule. The aim of the TPD study was to determine whether or not the molecule came off intact, and whether, when the second nitrogen deprotonated, it came off as H2 or H2O. The TD-XPS provided a far clearer idea of the progress of the desorption of the second layer and the deprotonation of the nitrogen. Finally, in order to try and understand the formation of this rather strongly bound bilayer structure we adsorbed 1-methyl uracil onto the surface, to test whether intramolecular hydrogen bonding played a significant role in the formation of the bilayer. These measurements suggest that the bilayer structure form in a very similar manner with the 1-methyl uracil, suggesting that the bilayer structure is not mediated by intramolecular hydrogen bonding but rather by interaction with the protruding bridging oxygens of the TiO2(110) surface.

During a subsequent beam time at the Berlin electron storage ring for synchrotron radiation (BESSY), TD-XPS was performed to study the formation of a 2D covalent network. The aim of the study was to try and understand the growth of the network with and without the presence of silver nanoparticles and as a function of molecular and nanoparticle coverage, which are expected to act as a catalyst for the formation of a more uniform 2D network. Additional synchrotron experiments on Cr tetraphenylporphyrin supported on Ag(111) and its interaction with molecular oxygen were also conducted during this period.

Finally, during these three months the fellow also pursued the benchmarking of the equipment available at the TUM for the acquisition of ARPES measurements by measuring the dispersion of the Ag(111) Shockley surface state; moreover, designs for the electronics to convert the metal evaporators present at the E20 group to be generalised for silicon evaporation were also put forward, specifically requiring a constant power, instead of constant current, source due to the variation of the resistivity of silicon as a function of temperature. Despite the premature ending of the SiliNano project the applicant does remain convinced of the scientific interest of 2D‑sheetmaterials, and as such the fellow aims to study the adsorption of a molecular species onto a graphene layer grown on iridium with intercalated cobalt and molecular adsorbates on boron nitride with Prof. W. Auwärter and Dr. F. Allegretti at the Technical University of Munich.

**PROJECT MANAGEMENT**

Prof. J. V. Barth and the project coworkers provided training and ongoing supervision to the fellow. All necessary infrastructure, comprehensive scientific research support and integration of the fellow are also progressed by the supervisor. The advancement of the project and the necessary actions have been discussed in meetings. Dissemination of the results including publications, attending workshops, conferences and seminars are coordinated.